

# Spin-rotation interaction in fullerite C<sub>60</sub>

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We report on the <sup>13</sup>C spin-lattice relaxation times in polycrystalline fullerite C<sub>60</sub> measured over the temperature range 295 K to 1000 K. At temperatures above 470 K, spin-lattice relaxation is dominated by the spin-rotation interaction. From the analysis of temperature dependence of  $T_1(^{13}\text{C})$ , the spin-rotation constant is determined using  $J$ - and  $M$ -models of rotational diffusion:  $C_J \simeq -51$  Hz,  $C_M \simeq -29$  Hz.

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## INTRODUCTION

When a molecule rotates, the motion of its nuclear and electronic charges produces alternative magnetic fields. These fields may then interact with nuclear spins in the molecule. The resulting spin-rotation interaction is one of the possible competing contributions to the mechanisms of nuclear spin-lattice relaxation in the gas and condensed phases [1]. The extraction of the contribution due to the spin-rotation mechanism solely from the spin-lattice relaxation is of interest in several ways. Firstly, it is especially useful to have a knowledge of the molecular reorientation correlation time  $\tau_\theta$  and the angular momentum correlation time  $\tau_J$  in order to differentiate between alternative models of molecular rotation, i.e., the rotational jump model versus the rotational diffusion one. While  $\tau_\theta$  can be determined reliably by a variety of methods,  $\tau_J$  is far less available to precise measurement. The fact that the interaction between nuclear spin and magnetic field generated by molecular rotation is a dominant mechanism for spin-lattice relaxation provides an excellent approach to the determination of  $\tau_\theta$ . Secondly, the spin-rotation constants can be used to find the paramagnetic part of the shielding tensor, and vice versa.

Fullerite C<sub>60</sub> is the only known solid that consists of quasispherical homonuclear molecules. At ambient temperatures, these molecules rotate quite fast, despite a very large moment of inertia,  $10^{-36}$  g cm<sup>2</sup>. Although the spin-rotation constant in C<sub>60</sub> is relatively small (25.6 Hz, as estimated from chemical shift), the spin-rotation interaction in this compound would be expected to significantly contribute to spin-lattice relaxation even at temperatures about 400 K [2].

<sup>13</sup>C NMR line shape and spin-lattice relaxation in fullerite C<sub>60</sub> have been studied in magnetic fields of 1.4 to 9.4 T at temperatures ranging from 100 to 340 K [3, 4, 5, 6]. These experiments clearly demonstrate that the <sup>13</sup>C NMR spectrum of fullerite C<sub>60</sub> in the range 100–

340 K is dominated by one type of magnetic interaction, namely, by <sup>13</sup>C magnetic shielding anisotropy, which determines both the line shape and  $T_1$ . We have recently described rotational dynamics in fullerite C<sub>60</sub> in terms of multiaxial discrete reorientations of C<sub>60</sub> molecules and suggested that the experimental manifestation of spin-rotation interaction C<sub>60</sub> should be noticeable at temperatures above 400 K [2].

Herein, we present the data in favor of this hypothesis. We report on the results of measuring spin-lattice relaxation time  $T_1(^{13}\text{C})$  and <sup>13</sup>C NMR chemical shift in polycrystalline fullerite C<sub>60</sub> at temperatures ranging from 295 to 1000 K and on the experimental manifestation of spin-rotation interaction. From theoretical analysis of the temperature behavior of  $T_1(^{13}\text{C})$ , we determined correlation times of the C<sub>60</sub> rotation angular momentum and the spin-rotation coupling constant of <sup>13</sup>C nuclei in a fullerite C<sub>60</sub> molecule.

## EXPERIMENTAL

A polycrystalline C<sub>60</sub> sample was obtained by crystallization from a toluene solution, washed with hexane, and annealed in vacuum at 200°C. HPLC showed that the content of oxides and higher fullerenes was less than 0.02%. XRD confirmed a high degree of crystallinity of the sample. The heat capacity of the same sample was measured by DSC in the range 285–675 K [7]. The values obtained were consistent with available data.

A C<sub>60</sub> powder (400 mg) was loaded into a quartz NMR tube 5 mm in o.d. and 50 mm in length, evacuated to a residual pressure of 0.1 mm Hg, and sealed. NMR measurements were performed on a Bruker MSL-300 spectrometer in a field of 7.04 T (75.4 MHz); an original high-temperature probe was used to cover the temperature range 295–1000 K. A furnace 50 mm long with the maximal outer diameter of 20 mm was designed with the use of two coaxial quartz tubes. A noninductively wound

heating element was placed in between these tubes. An RF coil was fixed at a zircon tube 50 mm in length, 7 mm in o.d., and 5.8 mm in i.d. The tube with a sample was positioned in the zircon tube. For thermal insulation of the furnace, quartz wool was used. At a sample temperature of 1000 K, the temperature of the probe cover was no more than 50°C. Forced cooling of the RF circuit was not used. Temperatures were calibrated with the use of a Chromel–Alumel thermocouple. The temperature reproducibility with allowance for the heat gradient was  $\pm 20^\circ\text{C}$ . NMR spectra were excited by a one-pulse sequence at a dead time of 4 ms and a pulse repetition time of 80 s; the number of scans, 100; scan width, 10 kHz; SI 16K and TD 16K. Chemical shifts were measured from  $\text{CHCl}_3$  (77 ppm with respect to TMS) as the external reference. Spin–lattice relaxation times were measured with the use of the saturation–recovery pulse sequence,  $(90_x - t_1 - 90_x)_n - \tau_2 - 90_y - 5T_1$ . The  $\pi/2$  pulse width was 9 ms,  $n = 100$ , and time delays  $\tau_2$  were from 1 to 500 s. Time  $t_1 = 100$  ms was optimized so that a signal upon saturation was absent. To construct the plots of signal amplitude versus delay time, 14 to 17  $\tau_2$  values were used. The  $T_1$  values were obtained through processing the amplitude– $\tau_2$  plots with the SIMFIT program (ASPECT-3000 software) with allowance for one-exponential magnetization recovery. Figure 1 shows a representative plot of signal amplitude recovery. Before

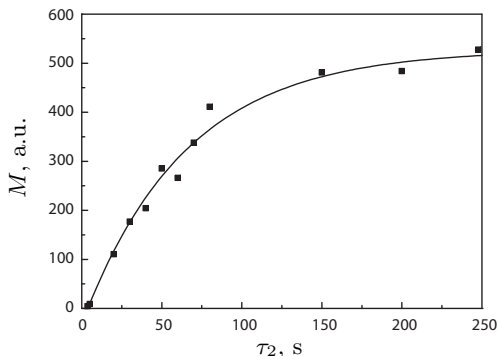


FIG. 1: Recovery of magnetization  $M$  (arb. units) of  $^{13}\text{C}$  spins in fullerite  $\text{C}_{60}$  at 863 K after the action of a saturating pulse train. The solid curve is described by the equation  $M(\tau) = M_\infty[1 - \exp(-\tau/T_1)]$  at  $T_1 = 59 \pm 5$  s.

each run, the sample was kept at a specified temperature for no less than 60–100 min. It took about 5 h to measure  $T_1$  at one temperature point. Before each run, the sample was allowed to cool to room temperature. The error in measurement of  $T_1$  was 7–10%.

## RESULTS

The  $^{13}\text{C}$  NMR signal of the sample studied at 295 K had a slightly asymmetric contour with a chemical shift

of  $143.6 \pm 0.2$  ppm and the line width at half-maximum of 3.6 ppm, which is consistent with the known data [3, 4, 5, 6]. With an increase in temperature to 800 K, the chemical shift linearly changes by only 2.5 ppm (Fig. 2) and the line width remains unaltered within the error of measurements and is presumably dominated by the field  $B_0$  inhomogeneity. In contrast to the line width and

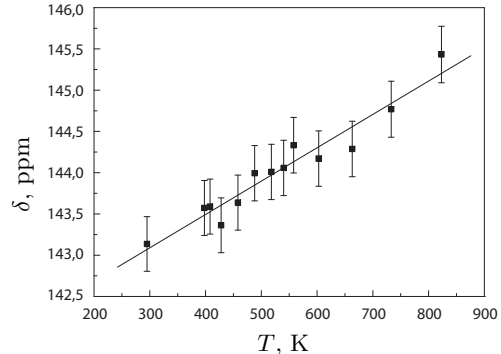


FIG. 2:  $^{13}\text{C}$  NMR chemical shift (ppm from TMS) in fullerite vs. temperature. Regression line:  $\delta = 141.8 + 4 \times 10^{-3}T$ .

chemical shift, the spin–lattice relaxation time  $T_1(^{13}\text{C})$  experiences noticeable changes in the temperature range studied (Fig. 3). Increasing temperature from 295 to

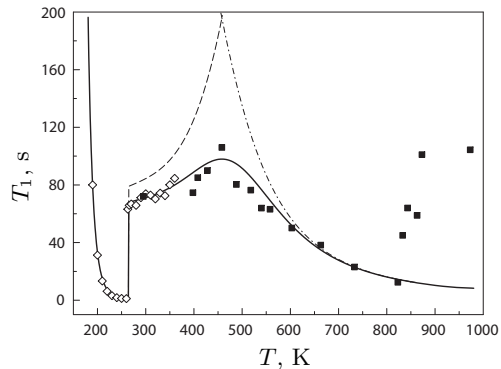


FIG. 3: Theoretical and experimental temperature dependence of spin–lattice relaxation time  $T_1(^{13}\text{C})$  in fullerite  $\text{C}_{60}$  at 190–1000 K ( $B_0 = 7.04$  T). Solid line: Calculated  $T_1$ . Dashed line: Contribution chemical shift anisotropy to  $T_1$ . Dot-dash line: Spin–rotation contribution. Symbols  $\diamond$ : experimental data of Tycko et al. [4] and Privalov et al. [6];  $\blacksquare$ : present work. Jump of  $T_1$  at 260 K corresponds to the reversible s.c.—f.c.c. phase transition.

473 K is accompanied by an expected slight increase in  $T_1$  from 77 to 107 s [2]. A further increase in temperature results in a smooth decrease in  $T_1$  to 12 s at 823 K, being a strong evidence that the dominating mechanism of  $^{13}\text{C}$  spin–lattice relaxation in fullerite changes with an increase in temperature from the magnetic shielding anisotropy mechanism at ambient and low temperatures to the spin–rotation mechanism at high temperatures. To the best of our knowledge, this is the first example of

realization of spin-rotation interaction in solid-state  $^{13}\text{C}$  NMR. At temperatures 830–900 K,  $T_1$  sharply increases to 100 s. In the range 900–1000 K,  $T_1$  is roughly temperature independent. The reasons behind this behavior of  $T_1(^{13}\text{C})$  at temperatures ranging from 830 to 1000 K are not clear. Note that the changes in  $T_1$  observed are reversible.

## DISCUSSION

### Chemical shift

The linear change in chemical shift observed with a change in temperature (Fig. 2) is caused by averaging  $^{13}\text{C}$  magnetic shielding over the rovibrational states of  $\text{C}_{60}$  molecule

$$\langle\sigma\rangle \approx \sigma_e + 2\sigma'_s\langle\Delta r_s\rangle + \sigma'_d\langle\Delta r_d\rangle, \quad (1)$$

where  $\sigma_e$  is the chemical shift constant at equilibrium state,  $\Delta r = r - r_e$  is the change in double ( $d$ ) and single ( $s$ ) bond lengths in  $\text{C}_{60}$ ,  $\sigma'_s = (\partial\sigma/\partial r_s)_e$ ,  $\sigma'_d = (\partial\sigma/\partial r_d)_e$ , and  $\langle\cdot\rangle$  denotes averaging over rovibrational states. In combination with the data on bond lengths in  $\text{C}_{60}$  at temperatures 4–295 K [8], Eq. (1) leads to the following relation:  $-400 = -12.4\sigma'_s + 3.5\sigma'_d$ . If we suppose that  $\sigma'_d$  in  $\text{C}_{60}$  is close to the one in ethylene (Table I), then  $\sigma'_s \simeq -20 \text{ ppm } \text{\AA}^{-1}$ , which is comparable with the magnitude of  $\sigma'_s$  in ethane.

TABLE I: C–C bond lengths, chemical shifts of  $^{13}\text{C}$  nuclei with respect to bare  $^{13}\text{C}$ , and their derivatives in ethane, ethylene, acetylene, and fullerene.

	$r(300 \text{ K})$ (\AA)	$\sigma(300 \text{ K})$ (ppm)	$(\partial\sigma/\partial r)_e$ (ppm \AA $^{-1}$ )
$\text{C}_2\text{H}_6$	1.545	183.1 <sup>a</sup>	−15 <sup>a</sup>
$\text{C}_2\text{H}_4$	1.335	66.76 <sup>a</sup>	−188 <sup>a</sup>
$\text{C}_2\text{H}_2$	1.205	121.35 <sup>a</sup>	−110 <sup>a</sup>
$\text{C}_{60}$	1.45, 1.40 <sup>b</sup>	61.0	−20, −188 <sup>b,c</sup>

<sup>a</sup>C. Jameson and H. Osten, *Theoretical aspects of isotope effects on nuclear shielding. Annual reports on NMR spectroscopy*, vol. 17 (Academic Press, London, 1986).

<sup>b</sup>The numbers refer to single and double bonds, respectively.

<sup>c</sup>Estimated according to the relationship  $-400 = -12.4\sigma'_p + 3.5\sigma'_h$  (see comments in the text).

### Spin-lattice relaxation time

The experimental temperature dependence of  $T_1$  can be adequately described in the model of molecular reorientations [2]. This model reproduces  $T_1(T)$  for both the low- and high-temperature phases up to 370 K, for which the experimental data are known. In the

low-temperature simple cubic phase,  $\text{C}_{60}$  molecules are assumed to jump between symmetry-equivalent positions about molecular symmetry axes, while in the high-temperature f.c.c. phase, reorientations take place also about crystal symmetry axes.

For the jump model,  $T_1$  due to chemical shift anisotropy is expressed in terms of correlation times for each type of reorientation axes [2]. With reasonable accuracy, this formula can be approximated by the formula for the diffusion rotation model with the effective correlation time  $\tau_\theta$ :

$$(1/T_1)_{CS} = \frac{3}{10}\omega_0^2\delta^2 \left(1 + \frac{\eta^2}{3}\right) \frac{\tau_\theta}{1 + \omega_0^2\tau_\theta^2},$$

where  $\delta = \sigma_{33} - \sigma$ ,  $\sigma = \sum_i \sigma_{ii}/3$ ,  $\eta = (\sigma_{11} - \sigma_{22})/\delta$  is the asymmetry parameter,  $\sigma_{ii}$  are the principal components of the shielding tensor, and  $\omega_0$  is the Larmor frequency. Values of these parameters for fullerite  $\text{C}_{60}$  were determined earlier [3, 4, 5, 6]:  $\sigma = 1.43 \times 10^{-4}$  (from TMS),  $\delta = -1.1 \times 10^{-4}$ ,  $\eta = 0.24$ . Here, we use  $\omega_0 = 2\pi \times 75.4 \text{ MHz}$ .

The decrease in  $T_1$  observed at 470–820 K can be assigned to the spin-rotation interaction, which becomes dominant in this temperature range. This relaxation mechanism is characterized by the angular momentum correlation time  $\tau_J$  [9, 10, 11]. In terms of so-called  $J$ - and  $M$ -models for rotational diffusion and in the limit  $\tau_J \ll \tau_\theta$ ,  $\tau_J$  and  $\tau_\theta$  for a spherical top molecule are related to each other as  $\tau_\theta\tau_J = I/6kT$  and  $\tau_\theta\tau_J = I/2kT$  for  $J$ - and  $M$ -models, respectively (where  $I$  is the moment of inertia of the molecule). The spin-lattice relaxation rate due to spin-rotation interaction is given by

$$(1/T_1)_{SR} = \frac{8\pi^2 kT}{\hbar^2} IC^2 \tau_J,$$

where  $C$  is the spin-rotation constant.

The resulting relaxation rate is  $1/T_1 = (1/T_1)_{CS} + (1/T_1)_{SR}$ . At temperatures lower than 350 K, the relaxation rate is dominated by the chemical shift anisotropy. Fitting the model data to the experimental data in this temperature range gives the kinetic parameters of molecular reorientations (Table II). These parameters are supposed to be also valid at higher temperatures. It is easy to verify that, in this case,  $\tau_J < \tau_\theta$  at temperatures below 900 K and, hence, the relation between these two quantities holds. The constant  $C$  can be readily determined from the position of the maximum of  $T_1$  at 360 K, where  $(T_1)_{CS} = (T_1)_{SR}$ . Since  $I(\text{C}_{60}) = 10^{-36} \text{ g cm}^2$ , we have  $|C_J| \simeq 51 \text{ Hz}$ ,  $|C_M| \simeq 29 \text{ Hz}$  for  $J$ - and  $M$ -models, respectively. The value of the spin-rotation constant obtained in the  $M$  model is in reasonable agreement with that derived from the chemical shift,  $-25.6 \text{ Hz}$ .

The model of molecular dynamics in fullerite  $\text{C}_{60}$  suggested adequately describes  $T_1(T)$  in the range 190–830 K. However, the most intriguing is the reversible effect associated with a sharp increase in  $T_1$  at 830–900 K,

TABLE II: Kinetic parameters of molecular reorientations in fullerite C<sub>60</sub> at 190–830 K in Arrhenius approximation. In the low-temperature simple cubic phase the molecules are assumed to jump about molecular symmetry axes. In the high-temperature f.c.c. phase reorientations about crystal symmetry axes are added.

$\tau_{0,\text{mol}}$ ( $\times 10^{-14}$ s)	$E_{\text{mol}}$ (kJ mol <sup>-1</sup> )	$\tau_{0,\text{cr}}$ ( $\times 10^{-10}$ s)	$E_{\text{cr}}$ (kJ mol <sup>-1</sup> )
0.85	27.45	0.10	0.83

followed by the constancy of  $T_1$  in the range 900–1000 K. One of the possible reasons can be a high-temperature phase transition [12], although high-temperature *in situ* studies of a C<sub>60</sub> powder by high-resolution XRD did not disclose a deviation from linearity for the volume expansion coefficient [13, 14]. This problem calls for further investigation. We hope to address this problem in the near future.

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